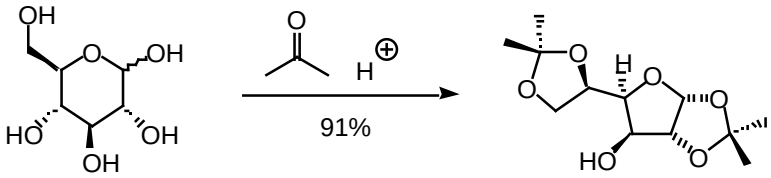
Carbohydrate Chemistry

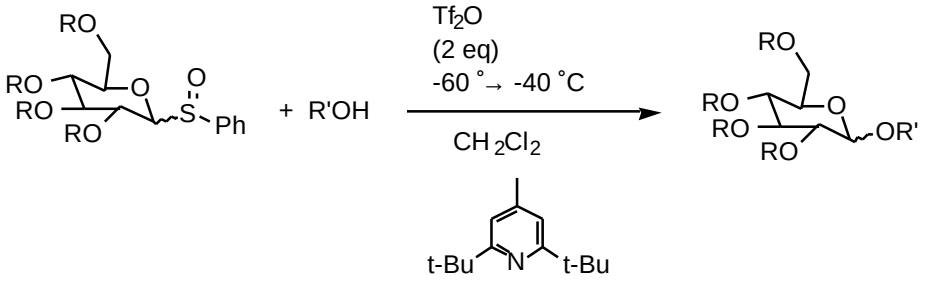
Organic Cumulative Exam
Saturday, May 8, 1999
9:00 AM- 12:00 noon
125I Chemistry

1. Provide **a complete** arrow pushing mechanism for the following transformation: **(20 points)**



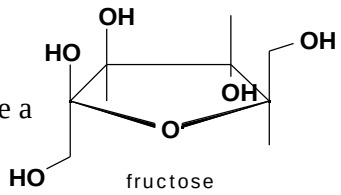
The synthesis of oligosaccarides is an important step on the way toward understanding the complex biological roles of these species. Professor Daniel Kahn and coworkers at Princeton have developed a number of useful methods for the construction of sugar-sugar linkages.

2. Propose a mechanism for the coupling reaction shown below. (**20 points**)



5. The furanose form of fructose, a ketohexose is shown below. Fructose gives a positive test with Fehling's reagent ($Cu(NH_3)_4(OH)_2$) a reagent, like Tollen's reagent which oxidizes an aldehyde to a carboxylic acid. It is used to determine whether a sugar is a "reducing sugar": Fructose is a reducing sugar. Answer the following questions. **(25 points)**

a. Give a mechanism for the conversions which will enable fructose to give a positive test with Fehling's reagent.



fructose

Answer the following regarding glucose.

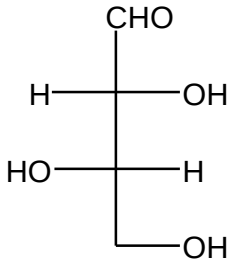
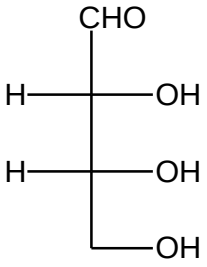
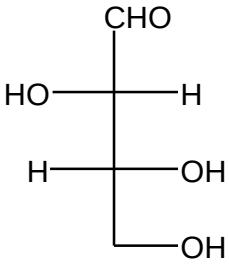
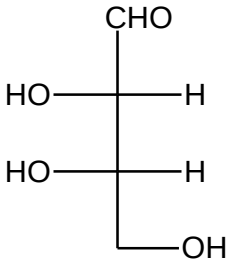
b. There are two important polysaccharides derived from glucose. What are they and how do they differ.

c. D-Glucose and D-manose both give the same osazone when reacting with phenylhydrazine. Give the Fisher projection formula for D-manose and give the structure of the phenylosazone.

6. Stereochemistry and Fischer Projection of Sugars (25 points)

See "Chemoenzymatic Synthesis of All Four Stereoisomers of Sphingosine from Chlorobenzene: Glycosphingolipid Precursors" by T. C. Nugent and T. Hudlicky. *J. Org. Chem.* **1998**, *63*, 510.

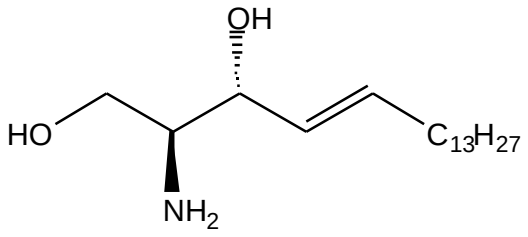
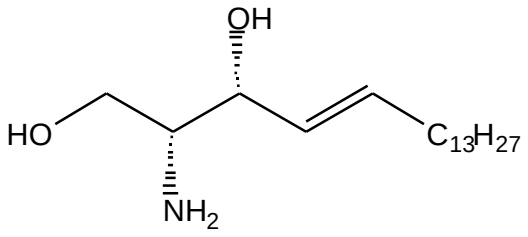
(a) Fischer projections are shown of the four stereoisomers of the four-carbon sugar (tetrose). Two of these tetroses are "erythroses" and two are "threoses." Two of these sugars are D-sugars and two are L-sugars. Under each structure, indicate to which class the respective structure belongs. Indicate the configuration of each chiral center using the R/S nomenclature. For clarity: The C-atom next to the formyl group is the C2 carbon.

			
Erythrose or Threose	Erythrose or Threose	Erythrose or Threose	Erythrose or Threose
D or L:	D or L:	D or L:	D or L:
R or S at C2:	R or S at C2:	R or S at C2:	R or S at C2:
R or S at C3:	R or S at C3:	R or S at C3:	R or S at C3:

(b) Produce a perspective drawing of the sugar shown to the very left in (a) in <u>two conformations</u> as follows: Draw the conformation used for the Fischer projection in the space to the left. Draw a conformation that is actually realized by that sugar in the space to the right. [Note: For the second perspective drawing there are several possibilities and any "local minimum" will do fine.]

Conformation adopted in Fischer Projection	An actual conformation:

(c) Fischer projections are shown of two stereoisomers of sphingosine. Indicate whether the sugars are "erythro" or "threo." Indicate whether the sugars are D- or L-sugars. Indicate the configuration of each chiral center using the R/S nomenclature. For clarity: The C-atom next to the primary alcohol is the C2 carbon.

	
Erythro or Threo	Erythro or Threo
D or L:	D or L:
R or S at C2:	R or S at C2:
R or S at C3:	R or S at C3:

(d) Consider the R/S nomenclature of D-erythrose and D-erythro sphingosine. Are they the same? Do they differ? What is the essence of what makes a molecule "erythro?"

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